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BY

R. E. BLAKE SMITH.

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TONING BROMIDE AND OTHER DEVELOPED SILVER PRINTS.

BY

R. E. BLAKE SMITH

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LONDON:
ILIFFE & SONS LIMITED,
1904

Iliffe & Sons Limited
London and Coventry.

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PREFACE.

THE following pages were written at the request of the Editor of *Photography*, and first appeared in the form of a series of articles in that journal. The subject of toning bromide papers is one about which much diversity of opinion exists.

A good many photographers will have nothing whatever to do with it. "Why," say these, "if you want coloured results, don't you use the carbon process?" The answer to this is that, while the carbon process is certainly the one yielding the best results in every way, yet, owing to its undoubted difficulties, it is not one which is suitable for universal employment. Some have said that they cannot see where the difficulties of the carbon process come in. They cannot have considered all the bearings of the subject. The enormous popularity which the bromide process enjoys shows how well it meets the wants of photographers.

As everybody knows, black and white are the rendering of a subject given by an ordinarily developed bromide print. Such a rendering is not suitable or pleasing for all subjects; and so, in order to give more scope to the bromide process, many methods of changing the normal tone have been proposed. Some of these processes are both easy and simple to carry out, and yield results about the permanence of which no fear need be felt; but of others the same thing cannot be said. Care is certainly necessary in choosing the particular toning process to be employed.

In what follows I have endeavoured in every case to indicate, as far as can at present be done, the probable effect each different process described in this book will have on the life of a print; and the advice I would offer to all who will accept it is only to employ those methods which yield results of which the permanence is above suspicion.

In conclusion, I can only express the hope that what I have written will prove of service to bromide workers.

I.—THE COLOUR OF THE ORIGINAL IMAGE.

BROMIDE and the similar papers with which the following pages will deal are those which are coated with an emulsion of gelatine and a silver haloid, or a mixture of silver haloids. When such an emulsion is exposed to light, a latent image is at first formed, which is not directly visible, but can be made to give rise to a visible image by the application of certain chemicals. These chemicals are known as the developer, and these papers are often spoken of as development papers.

Longer exposure to the action of light will produce a visible image; but practical photographers are only concerned with the invisible or latent image produced by a comparatively short exposure.

This is not the place to enter into the question of the nature of the latent image; but it may be said in brief that there are three or four theories which have been advanced as to its composition. One is that it consists of a sub-haloid of silver; another

that it consists of metallic silver—*i.e.*, in both cases a chemical decomposition is assumed to occur; while another, on the other hand, is that it consists of the silver haloid, or haloids chemically undecomposed but altered molecularly—*i.e.*, a physical and not a chemical change occurs. An extremely interesting paper by Dr. Luppo-Cramer on this subject is contained in "The British Journal Photographic Almanac" for 1903, pages 811-835. The sub-haloid theory is fully set out and expounded in Professor Meldola's "Chemistry of Photography" (Macmillan and Co.)

A photographic developer may be described as a chemically reducing solution, so made up and controlled that it exerts an action upon those portions of the sensitive compound which have been exposed to light, but does not appreciably affect the unexposed portions.

In order to obtain satisfactory results, the prints when completed should be of such a kind that—

(1.) The contrasts are suitably and pleasingly rendered.

(2.) The depth, or substance, of the

image is regulated to a pleasing and suitable degree.

(3.) The tone, or colour, of the image is good.

It is the last of these conditions which is the one particularly to be dealt with here; but since all the three are more or less bound up together, a few words must be said on the other two.

Commencing with the question of the production of black and grey tones on true bromide paper, the first point to be considered is the composition of the developer.

At one time ferrous oxalate enjoyed almost a monopoly for bromide paper development, but lately it has been very largely superseded by various other (phenolic) developers. Ferrous oxalate gives with suitable exposure a particularly good and rich black. It is a black which when the print is wet has in it a slight pervading tint of blue. The comparative excellence of different tones is, of course, purely a matter of taste; but I personally very much admire the results of ferrous oxalate development, and I find it very difficult quite to equal them with any phenolic developer I have used. All the

same, I think the almost complete abandonment of the iron developer shows sound judgment on the part of practical photographers. The bother and danger of using ferrous oxalate are much too great to be compensated for by a very slight gain in excellence of tone, even if this is admitted to take place.

A great number of excellent developing formulæ have been given. The following two are very good :

I.

Amidol	22	grains
Potassium bromide ..	5	,,
Sodium sulphite ($Na_2SO_3 7H_2O$)	$\frac{1}{2}$	ounce
Water	to 10	ounces

II.

Metol	16	grains
Hydroquinone	8	,,
Potassium bromide ..	6	,,
Sodium sulphite ($Na_2SO_3 7H_2O$)	$\frac{1}{2}$	ounce
Sodium carbonate ($Na_2CO_3 10H_2O$)	$\frac{1}{4}$	,,
Water	to 10	ounces

The amidol developer only keeps in good

condition for about two days after mixing.

These formulæ work well with all brands and qualities of paper; but it is a good general rule in the case of any particular brand of paper to follow exactly the directions issued therewith.

Such formulæ as the above are what are generally termed normal developers, *i.e.*, they are about the strongest developers which can with advantage be employed. The actual quantity of sodium or other soluble sulphite to be used is an important consideration. No risk of stains, caused by brown oxidation products of the phenol, *i.e.*, amidol, metol, hydroquinone, etc., should be run, and therefore a quantity of sulphite sufficient to prevent resinification from taking place must always be added. With the above formulæ, about three per cent. (thirteen grains to the ounce) is the minimum that can with perfect safety be used, and five per cent. will be found better.

With amidol, sodium sulphite acts as an accelerator as well as a preservative, and if it is reduced in quantity, sodium carbonate or some other suitable substance must be added to make up for the deficiency.

Five per cent. should not be much exceeded in any case, because sodium sulphite is a factor in the production at times of fog and certain stains—silver stains as opposed to oxidised phenol stains.

What happens is this: The sodium sulphite dissolves out of the emulsion some silver haloid, and forms a solution of a double sulphite of silver and sodium. The silver solution is easily reduced in the absence of sufficient potassium bromide by strong developing solutions. This produces general fog.

It is, of course, not the only way general fog can be produced—the non-actinically altered silver haloid is reduced *in situ* by too strong a developer, as can be shown by eliminating the chance of sulphite action. The production of fog through the action of sodium sulphite is, however, an important phenomenon which should be borne in mind by the bromide worker. The action can be observed by varying the amount of sodium sulphite in a normal developer containing no bromide, and in another way which will be referred to later. In the case of amidol, the above observation is, of course, no test by itself.

When the developer is of a slow-acting nature, yellow silver stains are produced if a large quantity of sulphite is present.

Too much potassium bromide must not be added, or the purity of the tone will be impaired. The quantity of this substance allowable varies with the constituents of the developing solution, especially with the particular phenol used. It is not necessary with all brands of paper to add as much potassium bromide as is contained in the formulæ already given; but it must be remembered that these are general formulæ. With these particular formulæ, the quantity of potassium bromide can be even increased without harming the tone in any way.

The colour of the silver image finally obtained on bromide paper depends, as everyone who has used it knows, not merely on the development, but on the exposure as well. When a normal developer is applied to an exposed bromide print, and brings out ample detail and ample but not too great density, and when also, after this has taken place, however long the print is subjected to the developer, no further silver is deposited except in the form of general

fog, such a print is said to have received a "correct exposure."

It may not be strictly true to say that no further density is gained by a print which has received a definite and limited exposure after a certain definite period of development. In the case of certain emulsions developed with certain developing solutions, at all events a kind of silver intensification is apparently set up, very likely due to some solvent action such as might be exerted by ammonia or by a soluble sulphite. The well-known experiments of Sir W. Abney and Dr. Eder must be here recalled to mind (see Meldola's "Chemistry of Photography," pages 175-176). However, for all practical purposes with all the commonly employed developers for bromide work, it is true that after a certain limited period of development, no further density is gained by the image, or what further density is gained is incommensurate with the amount of general fog produced.

A "correct" exposure may or may not give the representation and contrast required in the print. We must modify exposure and development to suit the result required.

Exposure must be shortened to increase contrast, and increased to decrease it. Unless we wish to develop right out, it is necessary to dilute the normal developer in order to give sufficient control over its action to the operator. Now, with "correct" exposure and normal development, the developing formulæ already given, and others like them, give very good black tones. On dilution, they also give excellent grey tones, correct or nearly correct exposure being given.

Dilution gives grey tones, because it enables us to stop development readily at any required point before too great density has been obtained. Keeping the exposure the same, a diluted developer will develop out a print to the same extent, or practically to the same extent, as a normal one, only it will, of course, take longer to do so. The contrasts, however, are slightly lessened, and the tone slightly altered. Probably the same amount of silver is deposited, but its state of molecular aggregation is somewhat different. The contrasts can be left unaltered by giving rather less exposure in the case of the dilute developer, but then the same amount of density cannot be obtained.

When, however, the exposure has to be much increased above the normal and a very dilute developer used, the final tone of the print is much altered; the pure black or grey is pervaded by shades of yellowish brown. Before discussing the question of improving such spoilt tones, the production of black images on gelatino-chloride, or gaslight, papers may conveniently be considered. These are very similar to bromide paper, but require rather different treatment in development.

Silver chloride is much more soluble in sodium sulphite solution than silver bromide, and this fact has to be remembered when dealing with the chloride, or chiefly chloride, papers. It has also to be remembered that the colour of the silver produced by the decomposition of silver chloride is much more readily varied than that produced by the decomposition of the other haloids.

A ferrous oxalate developer of proper strength and properly restrained is an excellent developer for gaslight papers, from a chemical point of view. The use of ferrous oxalate avoids all trouble caused by silver going into solution. Still, even here, it is

much more convenient to use one of the more modern developers.

The following will be found excellent:

Hydroquinone	30 grains
Metol	8 ,,
Potassium bromide	1 to 3 ,,
Sodium sulphite ($Na_2SO_3 7H_2O$)	200 ,,
Sodium carbonate ($Na_2CO_3 10H_2O$)	290 ,,
Water	to 10 ounces

Development with such a formula should be complete in about half a minute. If the potassium bromide be present in too great a quantity, the tone is rendered a greenish black, which is very unpleasant. A developer containing a larger quantity of such a rapid and powerfully acting reagent as metol would need more restrainer to prevent fog.

With correct or nearly correct exposures the above developer gives exceedingly fine tones with all brands of paper. The shadows are of a very rich black tone, which, when the print is wet, has a distinct shade of blue pervading it.

Gaslight papers are sold by most manufacturers in two qualities—one for hard nega-

tives and one for softer ones. It is certainly a good thing to avail one's self of these two qualities of paper as much as possible, but it should not be supposed from this that gaslight papers are not suitable for modified exposure and development. It is quite true that over-exposure and development with a dilute developer utterly spoils the tone for the time being, but this can be remedied afterwards, as will be shown in the next chapter.

Quite recently a method of obtaining pleasing contrasts in a bromide or gaslight print from a negative too " hard " to be dealt with in a normal manner was proposed by Mr. Sterry. Exposure is made so as to render suitably the detail in the high lights, *i.e.*, the shadows of the negative. If now development with a normal developer were carried out, the shadows (of the print) would be, of course, completely fogged up. Mr. Sterry, however, has found that by immersing the print between exposure and development in certain oxidising solutions, the contrasts of the print can be greatly lessened, and the overgrowth of the shadow density prevented. By this method, then,

similar results are obtained to those given by over-exposure followed by development with a dilute developer, only there is this important difference, that no alteration or at most only a slight alteration is brought about in the tone. Hence, none of the proceedings hereafter to be described for improving a poor tone need be gone through if Mr. Sterry's method is employed.

The practical details are few and simple. The print after exposure is thoroughly soaked in water (three minutes at least), and is then immersed in a dilute solution of potassium bichromate or chromic acid, the latter being better. The strength of the solution and the time of immersion vary with the effect desired. As a preliminary trial, one can ascertain the effect of an immersion of two minutes duration in a chromic acid solution containing two grains of pure chromic acid in every ten ounces of water. If potassium bichromate is used, a stronger solution is necessary than in the case of chromic acid, and it apparently will not work well with all brands of paper. It is best to wash the chromic acid or bichromate of potash out of the film before development, although

merely rinsing in water appears to suffice. Fifteen minutes' washing in running water will be found as a rule sufficient to eliminate all the chromium. In the case of bromide paper, an ordinary normal developer works very well after the chrome bath ; but in the case of gaslight paper, a weaker one will generally have to be used. The use of the normal gaslight developer will, at all events when the chrome treatment has been considerable, lead to fog production. It may very likely happen that a considerably weakened developer will have to be used with gaslight paper, and in this case, although a good tone is sure to be obtained, yet, in order to get the very best colour, the process to be described in the next chapter must afterwards be carried out. I have noticed in experimenting with Mr. Sterry's method that the chrome bath has sometimes an uneven action. This unevenness, which I have observed occurs more frequently with bichrome than with chromic acid, is the only objection which can be urged against the method. It is certainly one which all bromide workers should make a point of trying at the first available opportunity.

II.—THE COLOUR OF THE ORIGINAL IMAGE *(continued)*—REDEVELOPMENT OF THE IMAGE—WARM TONES BY DEVELOPMENT.

AS was shown in the previous chapter, it may very likely be the case that the colour of the image obtained on bromide or gaslight papers is either a greenish or rusty black or grey. The print as it stands in this case is useless. There are three or four methods of improving it by depositing on it some foreign substance, and these will be dealt with in their turn, but for the present consideration will be confined to a method of chlorinating the silver image, and then redeveloping it to silver again. This method is, on the whole, the best I know for the improvement of badly toned prints.

The procedure of bleaching the silver image of a bromide print and then redeveloping has been proposed for various purposes; but, as far as I am aware, it has not been proposed as a method of remedying "rustiness" and greenish blacks. It is certainly nothing like as well known as it deserves to be. Even images which are distinctly brown in colour can be rendered an excellent black or grey.

To carry it out, the prints should be first bleached in :

Potassium bichromate	90 grains
Concentrated sulphuric acid	200-400 minims
Sodium chloride (common salt)	1 ounce
Water	to 10 ounces

The prints are sufficiently bleached after an immersion of from five to ten minutes in this solution. The larger the quantity of sulphuric acid present the quicker the bleaching. After bleaching, the prints are washed in water till all the bichromate is washed out. Some people have found it necessary to give prints bleached in a bichromate bath such as the above an alum bath previous to washing, in order to facilitate the elimination of the bichromate or chromic acid. This is very likely due to the fact that the actual bath used contained too much bichromate and too little acid. At all events, I have never experienced any difficulty in washing the prints free from chrome stain ; ten minutes or a quarter of an hour in running water has always appeared to be long enough. However, if anyone is

troubled with the necessity of prolonged washing, the alum bath will be found a complete remedy.

The following is an excellent redeveloper :

Metol .. .. .. 45 grains
Sodium sulphite ($Na_2SO_3 7H_2O$) 130 ,,
Sodium carbonate .. 270 ,,
Water ($Na_2CO_3 10H_2O$) .. to 10 ounces

No potassium bromide should be used. It is very important in the case of the application of such a redeveloper to a chlorinated print to be on the look-out for silver sulphite complications.

The redeveloper must be so mixed as to dodge any chance of general fog being produced. The production of general fog in this case by the employment of an unsuitably mixed developer exhibits the fog producing action of sodium sulphite very well, for here no general fog can be produced except by silver passing into solution. The action of the metol redeveloper above given is apparently so powerful and rapid that any silver sulphite solution formed is decomposed *in situ* at once.

Ferrous oxalate (one part of a saturated solution of ferrous sulphate added to six

parts of a saturated solution of neutral potassium oxalate) is a very good redeveloper ; but, of course, needs an acid clearing solution after it. There is not the same objection to the use of an acid clearing bath in this case as in the case of primary development, because the operation is not performed in the dark room and there is no fixing bath to follow.

There is, of course, no harm in fixing a redeveloped print ; but it is quite unnecessary, and therefore better not to do so, for no unnecessary hypo should be ever introduced into a print. All that must be seen to is that redevelopment is complete ; and this can be confidently assumed to be the case when the print has been exposed to the action of the developer for a period of time twice as long as that taken to complete the visible effect. In case of doubt, however, fixing should be resorted to.

After redevelopment, the print, of course, must be thoroughly washed in water. The whole of the bleaching and redeveloping operations should be done in a normally lighted room.

Chlorinated bromide paper is readily re-

developed when quite unexposed to actinic light; but gaslight papers after chlorination are not so easily redeveloped under these circumstances. It does not appear that any definite and particular exposure to light is of importance, but a certain degree of exposure is advisable as helping the redevelopment; and, as I have just said, this can be most easily attained by performing all the operations in actinic light.

Silver iodide is not suitable for redevelopment, owing to its stability; and silver bromide, which is also more stable than the chloride and harder to reduce, does not give such pure blacks and greys.

Silver ferrocyanide with a suitable developer, as the metol formula above given, will yield good black and grey tones; but ferrous oxalate does not give such good results with silver ferrocyanide as it does with silver chloride.

A suitable bleaching solution for converting the silver of the image into silver ferrocyanide is:

Potassium ferricyanide	..	140 grains
Ammonium bromide	..	180 ,,
Water ..	..	to 10 ounces

After using this, the print must be washed n water till no yellow colour remains in the print. It is of course possible to bleach and redevelop a second time; but I have never observed any advantage, however, from doing so.

The chlorination and redevelopment of a silver image by the methods just advised, besides improving the tone, cause a slight but undoubted intensification. The state of the aggregation of the silver molecules is altered to some extent; and so not only is the colour of the deposit altered, but its body or covering power is also increased.

If P.O.P. be printed slightly darker than when gold toning is going to be resorted to, and then simply washed and fixed and again washed, it can be bleached in the bichromate-chloride bath, and then the silver chloride reduced to metallic silver with the metol redeveloper. The print finally obtained by this proceeding has a black silver image. The tones, however, as a rule, are not good, but can be improved by subsequent treatment. This method of dealing with P.O.P. is probably only of theoretical interest.

Having dealt with black silver tones, let us

pass to warm coloured ones. Here it is best to invert the former order of consideration, and to deal first with gaslight papers. The silver haloid contained in the emulsion on these papers is either wholly or chiefly the chloride.

Now, silver produced by the reduction of silver chloride, by varying the method of reduction, can be made to assume different states of aggregation, and so to appear in many differently coloured forms. Gaslight papers can be so exposed and developed as to yield images of many colours. The conditions for the production of warm-coloured images are over-exposure and development, with either a much diluted and restrained phenolic developer (metol, amidol, etc.), or else, which is much better, the ferrous citrate developer.

When warm-coloured prints are desired, the quality of paper used should be that adapted to give rather hard vigorous effects when black tones are produced on it from ordinary negatives. The exposure for warm colours must be made to suit the actual developer used. The contrasts obtainable must be made the first consideration, and not the tone. just as in the case where black tones are

produced. If with any developer suitable rendering of contrast cannot be obtained at the same time as the desired tone, the developer must be changed. Of course, with some negatives a longer exposure can be given than with others without spoiling the gradation of the contrasts.

As the longer the exposure is with any developer, the warmer becomes the tone, so the tone obtained from some negatives will be warmer than that obtained from others, the developer remaining the same.

The following is a developer which will be found suitable for warm-coloured images :

No. I.	Hydroquinone	30	grains
	Metol	8	,,
	Potassium bromide	1 to 1	,,
	Sodium sulphite ($Na_2SO_3 7H_2O$) ..	200	,,
	Sodium carbonate ($Na_2CO_3 10H_2O$) ..	290	,,
	Water	to 10	ounces
No. II.	Ammonium carbonate ..	$\frac{1}{2}$	ounce
	Ammonium bromide ..	$\frac{1}{2}$	,,
	Water	to 10	ounces

The following examples show the method of employing this developer :

BROWN TONES.—Exposure about four times normal.

No. I.	..	..	$1\frac{1}{2}$ ounces
No. II.	..	..	70 minims
Water	..	to	10 ounces

WARM BROWN TONES.—Exposure about six times normal.

No. I.	..	..	1 ounce
No. II.	..	..	190 minims
Water	..	to	10 ounces

VERY WARM BROWN TONES. — Exposure about eight times normal.

No. I.	..	..	$\frac{1}{2}$ ounce
No. II.	..	..	$\frac{1}{4}$,,
Water	..	to	10 ounces

RED TONES.—Exposure about ten times normal.

No. I.	..	..	160 minims
No. II.	..	..	100 ,,
Water	..	to	10 ounces

In using a ferrous citrate developer, the following solutions will be found serviceable :

STOCK SOLUTION I.

Ammonium citrate	..	3	ounces
Water	..	to 10	,,

It is as a rule best to filter this solution,

as the ammonium citrate generally met with is somewhat dirty.

STOCK SOLUTION II.

Citric acid	.. ..	3	ounces
Water	.. ..	to 10	,,

STOCK SOLUTION III.

Ferrous sulphate	..	$3\frac{1}{4}$	ounces
Con. sulphuric acid	..	25	minims
Water	.. ..	to 10	ounces

STOCK SOLUTION IV.

Sodium chloride (common salt)	.. .. ..	1	ounce
Water	.. ..	to 10	ounces

The following examples of the use of the above solutions are given :

BROWN TONES.—Exposure about four times normal.

No. I.	.. .. ..	3	ounces
No. III.	.. .. ..	1	ounce
No. IV.	.. .. ..	10	minims

No. IV. is best added by means of a dropping bottle.

WARM BROWN TONES.—Exposure about six times normal.

No. I.	.. .. ..	2	ounces
No. II.	.. .. ..	1	ounce
No. III.	.. .. ..	1	,,
No. IV.	.. .. ..	10	minims

The small quantity of sodium chloride in the above formulæ restrains development somewhat, and prevents a tendency to the production of uneven tones which generally shows itself in the absence of this substance. By increasing the amount of salt present in the developer, we can lengthen the exposure and obtain warmer tones, *e.g.* :

RED TONES.—Exposure about nine times normal.

No. I.	2 ounces
No. II.	1 ounce
No. III.	,,
No. IV.	100 minims

Yellowish tones can be got by both the phenolic and ferrous citrate developers by still further modifying the formula used from that required to yield red tones. Very few, if any, are, however, likely to care for yellowish tones.

If colder tones are desired than are given by the first formula, the ammonium citrate solution can be partially replaced by a saturated solution of neutral potassium oxalate. Instead of using three ounces of ammonium citrate, two and three-quarter ounces are used, and from one-eighth to one-quarter of an

ounce of the potassium oxalate solution added. The exposure in this case will be about three times the normal. No clearing bath is necessary with any of these citrate or citro-oxalate formulæ, but the prints must be well washed in water before fixing.

In an article in *Photography*, April 25th, 1903, page 407, attention was called to the fact that by substituting in the normal developer acetone sulphite for sodium sulphite, warmer tones can be obtained. A formula giving warm black tones with gaslight papers is :

Edinol	32	grains
Hydroquinone	32	,,
Acetone sulphite ..	96	,,
Tribasic sodium phosphate	512	,,
Potassium bromide ..	5	,,
Water	to 10	ounces

The production of warm tones by development on gaslight paper is quite an easy and satisfactory process ; although, as is only natural, it requires a little practice at first before the best results can be obtained. In the case of true bromide papers, however, it is not easy to obtain really warm tones in this manner.

It is easy enough to obtain warm black tones if such are admired. Suitably extended exposure and restrained development (*i.e.*, development with an abnormally large quantity of potassium bromide in the developer) will yield such tones ; but there is a danger, at all events in the case of some developers, of getting greenish results. The use of acetone sulphite seems to be the best plan at present available.

Mr. Wade in the above quoted article gives one of the best formula yet given for this purpose. It is :

Edinol	.. 20	grains
Acetone sulphite	.. 120	,,
Potassium carbonate	.. 150	,,
Water	to 10	ounces

Another formula on the same lines which works well is :

Adurol	.. 30	grains
Potassium bromide	.. $2\frac{1}{2}$	,,
Acetone sulphite	.. 135	,,
Sodium carbonate ($Na_2CO_3 10H_2O$)	270	,,
Water	to 10	ounces

The exposure must be varied to suit the tone as much as possible. Brown tones can

be obtained on true bromide paper by using the metol-hydroquinone ammonium carbonate developer given above. As an example :

No. I.	..	..	..	4 ounces
No. II.	..	..	..	¾ ,,
Water	..	..	to	10 ,,

will serve. About four times the normal exposure is required. The ferrous citrate developer may also be employed.

The method of obtaining brown tones on true bromide paper by development has not been much worked with, and not much is apparently known about it. All I can say is that in my hands the method has never yielded pleasing results, and I do not think it is of much practical value. Only hard negatives are suitable for producing brown prints.

Some attempts at different times have been made to obtain warm tones on bromide and gaslight papers by bleaching the black or grey silver image to silver chloride, and then redeveloping with a developer of the kind used for producing warm tones on gaslight paper by primary development. The method certainly, on the face of it, looks very promising, but very little has come of it so far.

Gaslight papers appear to give the best results.

Probably the lasting quality of a bromide print which has been carefully prepared and washed is much underrated by a good many people. A print normally developed from a rapid coarse-grained emulsion will certainly keep in splendid condition under ordinary circumstances for a great many years. Future experience will alone determine exactly how many. Though we cannot at present say anything very definite, there is good reason for believing that the probable life of a print will vary with the size of the silver particles forming the image. Certainly, the smaller the particles the more easily is the image acted on by chemical reagents. When normal development has been carried out, following a normal exposure, the size of the silver particles varies with the grain of the emulsion. With such prints, therefore, the lasting properties will probably vary with the emulsion from which they have been made. The warm-toned images produced by modified exposure and development, being of finer grain, will in all probability be found to be inferior in permanency to the normal black ones.

III.—GOLD AND PLATINUM TONING.

TONING the black or grey silver image on bromide or gaslight papers with gold is very seldom resorted to, as it is generally considered that as a rule nothing can be gained thereby. Gold is deposited on a bromide print in the blue-coloured state, and so the effect of gold toning is to render the tones much bluer than before.

Now, when the original tone is a good pure black or grey, most people will consider that, so far from any improvement being brought about by making it more blue in character, exactly the opposite is the case. However, the method can be advantageously employed when the print is in any way rusty or greenish in colour. Here it is best to employ in the first instance the redevelopment method advocated in the second chapter, and only to resort to gold toning if it should prove necessary after this has been done. In actual practice, redevelopment by itself will very seldom fail to yield a most satisfactory tone.

I do not mean to imply that gold toning is not a good method to employ. It is certainly a good method, only there is a danger of getting too blue a tone.

We noted in the preceding chapter that a print on P.O.P., simply fixed, could, after washing, be bleached and redeveloped so as to give a black image. The colour of the silver is in this case not as a rule satisfactory, but it can be put right by toning slightly with gold. A stronger solution of gold must be used with bromide prints than when ordinary P.O.P. prints are toned in the same manner. The coarser grain of the bromide print causes the inter-action between the gold compound and the silver to be much slower than in the case of P.O.P.

The ammonium sulphocyanide bath is usually recommended. To employ such a bath it is convenient to make up the following stock solutions :

I. GOLD STOCK SOLUTION.—One 15 grain tube of gold chloride in 5 ounces of water.

II. AMMONIUM SULPHOCYANIDE STOCK SOLUTION.—150 grains in 5 ounces of water.

One part of I. is added to one part of II., and the mixed solution allowed to stand till it is colourless. This solution is best diluted to half or even quarter strength, except when we wish to get a very blue tone.

After gold toning has proceeded to the

desired degree, the print should be washed in water and then fixed, and after this well washed again.

By resorting to gold toning in the case of gaslight papers on which a red silver image has been developed, a series of colours passing from red through purple to blue can be easily obtained. The bath generally recommended for this purpose is the well-known *sel d'or* solution, the formula for which is given below. A small quantity of sodium carbonate should be added, because otherwise a deposit of sulphur will at first occur. The precipitation of sulphur appears to be complete in about three hours; and it may be that, if the bath is allowed to stand for at least that time, no danger will arise. Still, there is a pretty generally felt suspicion that in such a case all the depositable sulphur does not come down in the first instance, but that it will be brought down by the attraction of the silver image, or perhaps of the gelatine, which has unfortunately the power of absorbing sulphur to some extent. The matter is not clear by any means, and so some soda should certainly be added. In this case the bath becomes quite free from objection.

GOLD STOCK SOLUTION.—One 15 grain tube of gold chloride in 11½ ounces of water.

SEL D'OR BATH.

Sodium carbonate .. ($Na_2CO_3 10H_2O$)	45	grains	
Hypo	2½	ounces	
Gold chloride solution ..	3	,,	
Water	to 10	,,	

This bath keeps well, and is replenished with fresh gold as required. In toning the red silver prints, care is needed to prevent over-toning, as the wet print is very deceptive.

An interesting method of toning bromide prints with gold was recently published by M. Le Mée in the *Photo-Revue*. The prints are first bleached in a bichromate-chloride bleacher—the one given in my last chapter will serve very well—and are then, after washing, exposed to light in a solution of sulphurous acid. A suitable solution is:

Sodium sulphite ($Na_2SO_3 7H_2O$)	40	grains
Sulphuric acid (concentrated)	12	minims
Water	to 10	ounces

The sodium sulphite is dissolved in the water before adding the acid. Substances other than sulphurous acid can be used, such as

citric acid, an alkaline citrate, or potassium nitrate; but sulphurous acid is much the best. On exposure to light in the above solution, the image reappears fairly rapidly. When it is sufficiently reprinted out, the paper must be washed for a few minutes, and can be then toned with gold.

It is claimed that the image thus obtained is much more favourable to gold toning than the original one. I cannot say that I have found much advantage in this proceeding as applied to gold toning, but it is certainly an interesting method which some may find advantageous. The action of the sulphurous acid is no doubt that of a chemical sensitiser —it absorbs chlorine, and so helps the action of light. If the image is too weak after fixing (which with these gold toning processes must never be omitted, except, of course, when a combined bath is employed), this shows that the exposure to light has not been long enough.

On exposing to light till apparently no further action occurs, and then after washing, either fixing or treating with a developer to get rid of any chloride or sub-chloride remaining, a dark purple silver image is obtained in

the case of bromide or gaslight papers, and a yellow one in the case of P.O.P. The purple images of the wet bromide and gaslight papers become almost black when the prints are dry.

Toning bromide or gaslight prints with platinum is not as a rule an advantageous proceeding; but, as in the case of gold, it may be used to cure rustiness and similar ills. A suitable solution may be made by dissolving about two grains of potassium chloroplatinite in one ounce of water and adding two or three drops of concentrated nitric acid. After toning, the print is washed in water, and then fixed. The colour of the deposited platinum is black.

Several attempts have been made to improve the platinum toning solution by adding to it certain other substances. Cupric chloride, ferric oxalate, potassium ferric oxalate, and mercuric chloride were proposed by the late Mr. W. B. Bolton (*British Journal of Photography*, November 9th, 1894). Mr. Bolton came to the conclusion that mercuric chloride was much the most suitable substance for this purpose.

In the case of the addition of mercuric chloride, the mechanism of the reaction is

probably this: Mercuric chloride bleaches the silver image forming silver chloride and mercurous chloride, and then the mercurous chloride so formed reacts with the platinous chloride, forming mercuric chloride again, and platinum is deposited. The image consists of silver chloride and platinum, together with an amount of mercurous chloride depending on the difference of the velocity of the action of platinous chloride on mercurous chloride, and the bleaching action of the mercuric chloride on the silver. There is also, of course, present in the image an amount of unaltered silver, depending on the stage to which bleaching has been carried.

A sepia tone is given to a bromide print by such a method; but it appears to be more due to the chlorides present than to the platinum, for it is destroyed in the fixing bath, and the print much weakened.

As to the permanence of prints toned by this method, little reliance can be placed thereon. It is certainly desirable in this case that the word platinum should not deceive. It must be said, however, that, although there are no doubt very suspicious points about such an image, yet in actual practice

many prints toned in this way have been found to last much better than one would have thought. It appears that the silver chloride is only very slightly affected, if at all, by light. This is curious, and is due to its molecular state being influenced by the mercurous chloride. The actual composition of the image is certainly a somewhat variable one, and so the degree of permanence possessed by different prints will vary. The method yields prints undoubtedly more open to attack by sulphuretted hydrogen than is an untoned bromide print, and as there are far better and more certain methods of obtaining a sepia tone, it would certainly appear most inadvisable to employ this one.

Mr. C. W. Somerville states that the composition of the bath should be exact in its details in order that a good tone may be obtained.

His formula is :

Potassium chloroplatinite		2 grains
Mercuric chloride	..	1 grain
Citric acid	.. ..	9 grains
Ten per cent. solution of potassium bromide	..	2 minims
Water	.. .. to	10 ounces

After the desired tone is gained, the print is washed in water, and is then complete. Fixation, for the reason above given, must not be resorted to. Mr. Somerville has advocated applying a developer to the toned print as a method of intensification. The developer reduces the silver chloride and mercurous chloride to silver and mercury. The metol redeveloper given in the previous chapter is suitable.

IV.—FERROCYANIDE COLOURS.

IF the silver image of a bromide or similar print is subjected to the action of a soluble ferricyanide (say potassium ferricyanide), silver ferrocyanide and potassium ferrocyanide are formed. There may be other subsidiary reactions occurring under certain circumstances, but these need not be considered here. Potassium ferrocyanide is soluble and of a pale yellow colour ; but there are other metals which form a soluble ferricyanide and an insoluble and strongly-coloured ferrocyanide, and by employing a solution of the ferricyanide of such metals, we obtain images of various colours. White insoluble silver ferrocyanide always forms part of the image unless it is specially removed.

As to the degree of permanence possessed by prints treated in this manner, it is difficult to speak with certainty. It is generally held that one of the chief dangers against which silver prints have to contend is the presence of small traces of sulphuretted hydrogen in the air. Now, sulphuretted hydrogen acts much more readily on a ferri-

cyanide-toned image than on a plain silver one; in other ways also the stability of the ferrocyanide compounds falls a good deal short of that of metallic silver, and so it would certainly seem that the risks against the life of the print are very considerably increased by this toning process. Sufficient practical evidence has not yet been accumulated to enable a fair judgment to be passed on this subject.

The ferricyanides chiefly employed for toning purposes are those of uranium, copper, and iron; and by their agency a great many tones may be obtained.

A suitable uranium bath is:

Uranium nitrate	..	12 grains
Potassium ferricyanide		6 „
Glacial acetic acid	..	150 minims
Water		to 10 ounces

This bath will not keep long, and so must be made up as required. Those who do not care to weigh out their own chemicals will find it convenient to keep in stock ten per cent. solutions of uranium nitrate and potassium ferricyanide, and to take for the toning bath:

Ten per cent. solution of uranium nitrate	.. 120 minims (2 drams)
Ten per cent. solution of potassium ferricyanide	60 minims (1 dram)
Glacial acetic acid	.. 150 minims
Water	to 10 ounces

The addition of the acetic acid is necessary, because the uranium ferrocyanide deposit is very easily attacked by alkalies; even ordinary hard tap water will slowly dissolve it.

The range of tones obtained with the uranium bath is very wide. The cold black silver image gradually changes to a warm black, then a dark brown, and afterwards passes through various shades of brown and reddish brown to a bright red.

The print is taken out of the solution when the desired colour has been reached. It is best to wash it in two or three changes of dilute (about one per cent.) acetic acid. After this, the print is washed in several changes of water. The washing in water must not be prolonged, or else the image will suffer. It should not occupy more than about a quarter of an hour, and at the end of this time the whites should be quite clear.

If, however, the whites are not clear by then, a very slightly alkaline solution can be used to expedite matters. Ammonia solution or ammonium carbonate are the alkaline substances generally used for this purpose, but caustic soda does very well. What is important is to use whatever alkaline substance is used in *very* dilute solution. The image, of course, will be somewhat reduced by this proceeding.

Another method of clearing the whites, which is perhaps safer to use as far as immediate results are concerned, but which may possibly be followed by undesirable consequences, is to immerse the print in a solution of ammonium sulphocyanide of about one per cent. strength. In this the whites will clear rapidly, and the rest of the print will be considerably brightened in colour. The brightening in colour is evidently due to the action of the ammonium sulphocyanide on the silver ferrocyanide, some of the latter being dissolved out. I do not know whether the ammonium sulphocyanide leaves behind any insoluble compound which would tend to shorten the life of the print ; but I do not think it does. After treatment with ammo-

nium sulphocyanide, the print should be washed in two or three changes of water, and then in several changes of dilute acetic acid, and finally again in three or four changes of water. No traces of ammonium sulphocyanide must be left in the print.

It has been proposed to treat a uranium toned print with hypo solution in order to brighten the tone by dissolving out some or all of the silver ferrocyanide. The result is no doubt attained easily enough, but how about the subsequent elimination of the hypo? A uranium-toned print cannot be washed for long in ordinary tap water, as this slowly dissolves away the image. An acid solution is not available in the case of hypo; and so if hypo be used, it would appear to be necessary to wash after its application in distilled water.

The following solution is said to yield excellent results, and to be less likely to produce stains than the ordinary one:

Lead nitrate	.. ..	7 grains
Potassium ferricyanide		20 „
Uranium acetate	..	15 „
Citric acid	.. ..	75 „
Ammonium chloride	..	3 „
Water	.. ..	to 10 ounces

I have myself obtained very good results with this formula when experimenting with it. After toning, the print must be washed as before.

Dr. Mills recommends treating uranium-toned prints after their final washing with a five per cent. solution of white dextrine containing a trace of glycerine. The prints are soaked for five minutes in this solution, and then drained and dried. It is claimed that the permanency of the toned prints is considerably increased by this process.

Copper ferrocyanide is a brownish red substance insoluble in water. The ferricyanide is also insoluble in water, but soluble in the solution of certain salts. Some years ago ammonium carbonate was often recommended as a solvent for copper ferricyanide. However, it was not until Mr. Ferguson pointed out the advantage of using alkaline citrates for this purpose that the copper ferricyanide method became of any real practical use. There are a good many solutions which dissolve copper ferricyanide and not copper ferrocyanide; but the alkaline citrates alone give solutions which will not stain the print, and are really satisfactory.

The following formula will be found to work very well :

Potassium ferricyanide		45 grains
Potassium citrate	..	1 ounce
Copper sulphate	..	55 grains
Water	to	10 ounces

or for those who like stock solutions :

Ten per cent. potassium ferricyanide solution..		1 ounce
Twelve per cent. copper sulphate solution	..	1 ,,
Twelve and a half per cent. potassium citrate solution		8 ounces

The colours obtained vary from a warm black through reddish-browns to red. I have never obtained a really good sepia tone with the copper ferricyanide bath ; the results have always been too red. After the desired tone has been obtained, the print is taken out of the toning solution and washed in running water for about twenty minutes. The image is attacked by alkalies and even by tap water just as the uranium-toned image is, but not nearly so readily.

If, as will sometimes happen with certain brands of paper, the high lights are somewhat

stained to a faint pinkish colour, they can be cleared with a dilute alkaline solution, as in the case of uranium stains; or the stains can generally be prevented by somewhat increasing the amount of the potassium citrate in the above formula.

Copper ferricyanide-toned prints can be brightened by the use of hypo, like the uranium-toned prints. Here also I consider it necessary to use distilled water for the final washing, although not so necessary as in the uranium case.

By means of a solution of ferric ferricyanide, a blue tone can be obtained due to the formation of ferric ferrocyanide (Prussian blue). In order to prevent the formation of a certain quantity of ferrous ferricyanide, which, not being quite insoluble, "runs" to some extent, it is necessary that the solution should contain some nitric acid.

The following is a good formula:

Potassium ferricyanide..	45 grains
Concentrated nitric acid	24 minims
Ferric ammonium citrate	22 grains
Water .. .. to	10 ounces

or in stock solutions:

Ten per cent. solution of potassium ferricyanide	1 ounce

Five per cent. solution of ferric ammonium citrate	1	ounce
Five per cent. nitric acid solution	1	„
Water	to 10	ounces

The above bath can be diluted with water if it be found to work too quickly. When the desired tone is obtained, the print is well washed in running water until the whites are clear. As a rule, prints toned with this bath should be washed for about twenty minutes. The use of the ferric ferricyanide bath as a cure for rusty prints has been suggested.

By combining the iron and the uranium baths, green tones may be obtained. The following can be tried:

Potassium ferricyanide..	45	grains
Concentrated nitric acid	24	minims
Ferric ammonium citrate	22	grains
Uranium nitrate ..	22	„
Water	to 10	ounces

or in case of stock solutions being employed:

Ten per cent. solution of potassium ferricyanide	1	ounce
Five per cent. solution of nitric acid (concentrated)	1	„

Five per cent. solution of uranium nitrate	..	1 ounce
Five per cent. solution of ferric ammonium citrate		1 „
Water	to	10 ounces

The proportions of the iron and uranium salts can be somewhat altered to suit the tone, and the bath can be somewhat diluted if desired. The washing after this bath must not be prolonged, but must be carried out as recommended for a uranium-toned print. Another method of obtaining green tones is first to tone a print red in the uranium bath, and then to treat it with:

Ferric chloride		10 grains
Hydrochloric acid (concentrated)		10 minims
Water	to	10 ounces

After this treatment, it is washed at first in two or three changes of dilute hydrochloric acid (about 0.5 per cent.), and then in three or four changes of water.

Another method of obtaining green tones is to tone the print slightly blue in the iron bath, and then after washing to immerse in a solution of chromic acid about one per cent. strength (four and a half grains to the

ounce). The method requires a considerable degree of skill to enable one to judge accurately the right depth of (silver) image to be obtained originally and the right point at which to stop the iron toning. The green colour is probably produced by a combination of the blue ferric ferrocyanide and yellowish silver chromate formed by the action of the chromic acid on the unaltered silver image. After the chromic acid bath, the print is washed for about a quarter of an hour in running water. If, however, it be found that the chromic acid cannot be washed out in this time, the print should be immersed for a few minutes in a saturated solution of alum before being washed in water.

By toning first in the iron bath to a blue tone, and then, after washing, in the copper, violet tones can be obtained.

Of late a certain number of facts have been brought to light, which seem to show that the previous treatment—development chiefly—has a good deal of influence on the subsequent toning by ferricyanide and other methods. The toning properties of the different brands of paper have also been recognised as often being to some extent

different. It is too early as yet to say anything very definite on this subject. Amidol appears to be the developer best suited for prints when toning is going to be carried out afterwards. However, it has been stated that in the case of uranium toning, the previous employment of amidol tends to produce stains, although there is even in this case testimony in its favour. I myself have never found amidol specially liable to give stained whites with uranium toning; but those who have been troubled in this way may perhaps find it to their advantage to try a developer made up with hydroquinone alone, as I have seen it stated that such a developer is the most suitable one to precede uranium toning.

With the uranium bath and some others, parts of the image will sometimes take the toning deposits more slowly than other parts, and so unevenness of tone will be produced unless the action is allowed to go to the full extent. A remedy which has been recommended, and one that is at all events very often efficacious, is to bleach the image to the chloride, and then to redevelop. The metol redeveloper given in a previous chapter

may be used; but ferrous citrate seems to be the best under these circumstances.

Perhaps the best method of ferricyanide toning would be one similar to that advocated by Le Mée for gold toning, as described in the previous chapter. Such a method would naturally be elaborate and somewhat laborious; but it might enable more dilute solutions of the ferricyanides to be used than is ordinarily the case without prolonging the time of toning, and so might tend to the avoidance of all stains.

V.—SULPHURETTING THE SILVER IMAGE. A.—Direct Methods.

IT is now I think generally admitted that the best methods of obtaining brown tones are those in which the silver image is converted into one of silver sulphide. As Sir W. Abney has pointed out in this connection, silver sulphide is about as permanent a compound as can exist; and an image composed of this substance must be regarded as a very permanent one. I believe that a sulphuretted print is possessed of somewhat better lasting properties than one having a plainly developed silver image upon it.

An image consisting of pure silver possesses, when its production has in all respects been properly carried out, excellent keeping qualities. We all know, however, that silver tarnishes in the presence of sulphides; and, of course, silver sulphide, to the formation of which the tarnishing is due, does not. Silver ornaments and plate become tarnished, especially under damp atmospheric conditions, by prolonged exposure to the

traces of sulphuretted hydrogen in the air, and the silver image of a print must to some extent share the same fate. By this I do not mean to imply that the silver image of modern bromide papers is *readily* attacked by the atmospheric sulphuretted hydrogen. Fortunately, the very reverse is the case, as will be seen presently, and this fact must be accounted to the bromide process for excellence.

Besides the presence of traces of sulphuretted hydrogen in the atmosphere, another cause of the slow deterioration of silver prints due to the action of hydrogen sulphide is the decomposition of the emulsion vehicle when that vehicle, as is the case with gelatine or albumen, contains sulphur.

However, these are very slowly-acting causes of fading, as is also the gradual failing of the actual paper on which the emulsion is spread, to which, of course, all prints are liable.

When prints possessed of a pure silver image or one of silver and gold or platinum fade and deteriorate quickly, *i.e.*, at the end of a very few years, it may be taken as certain that the cause of such fading is the

presence of chemical impurities—generally traces of hypo not completely eliminated after fixing. Any trace of hypo not washed out, in so far as it may cause sulphuration of the image, will affect a plain silver image, but not one of silver sulphide; but, in so far as it may lead to the staining and general deterioration of the emulsion vehicle or paper support, it will equally affect all kinds of prints.

The practical methods of sulphuretting a silver image may be considered under two heads:

(I.) Direct Methods.

(II.) Indirect Methods.

The direct methods consist of treating the print with a solution which converts the silver image directly into one consisting of silver sulphide. Sir W. Abney suggested some years ago that bromide prints should be treated with a solution of a soluble and suitable metallic sulphide, or of sulphuretted hydrogen.

The method was suggested, I believe, chiefly at all events, for the purpose of obtaining warm blacks rather than brown tones. With some of the slower bromide

papers and with gaslight papers the method may still prove useful for producing warm blacks. With no brand of gaslight or bromide paper is it suitable for the production of really warm tones. With the majority of the brands of bromide paper at present on the market, it is not suitable even for the production of warm blacks, as the action of the sulphuretting solution is so very slow. This is a very interesting fact, as bearing on the question of the stability of the bromide print.

The only direct sulphuretting solution which is at the present time commonly employed is one containing a mixture of hypo and alum. If alum be added to a solution of hypo, a white precipitate is slowly thrown down. This precipitate will vary according to temperature, and also according to the time which has elapsed after the mixture was made. At first it consists of sulphur and aluminium hydrate in something like equal proportions, but after a time the sulphur greatly preponderates. The toning process can be looked upon as due to the agency of nascent sulphur.

Different workers use somewhat different formulæ. The following is of about the com-

position usually employed:

Hypo	.. .. ..	1½ ounces
Alum	.. .. ..	70 grains
Water	.. .. to	10 ounces

Dr. Baekeland, by whom, I believe, the bath was in the first instance suggested, and to whom most of the exact knowledge we possess about its properties is due, recommends a somewhat stronger solution:

Hypo	.. .. ..	2 ounces
Alum	.. .. ..	200 grains
Water	.. .. to	10 ounces

In making up such solutions as the above, it is best to dissolve the hypo in water first, and then slowly to add the alum, stirring during the operation. The solution is then put into a bottle and allowed to stand for about two or three days at least. It is then heated up to about 130° F. with some old and useless prints, or else with the addition of a very small quantity of silver nitrate. The solution should remain at about 130° F. for an hour or so, and then after cooling it is ready for use.

This last proceeding is known as "ripening" the bath, and it must not be omitted. The above process can only be considered as

a minimum of what ought to be done in this respect.

The quickest results are obtained by employing the bath at as high a temperature as the film of the paper will stand—generally about 120° F.; but it is now generally admitted that better results can be obtained at a lower temperature. I do not think the temperature of the bath should exceed 80° F. to 90° F., and many people prefer to use it at ordinary atmospheric temperatures.

The time of toning will vary with the brand of paper used, the previous history of the print (method of development, etc.), and the temperature of the bath; it may be less than half an hour, and more than three days. It is generally admitted that, other things remaining the same, prints which have previously been developed with an amidol developer tone more readily than any others.

If the bath is used at temperatures above the ordinary temperature of the atmosphere, the print before immersion therein should receive an alum bath. In this case, the print should be washed between fixing and alum, and again for a short time after the alum.

It is best not to put the print straight into the hot solution, but slowly to raise the temperature of the bath to the required point after the print is in. After toning is complete, the print is taken out of the bath, and if this is hot, allowed to cool on the hand for a minute or so, and is then washed in running water. It is best at this stage to wipe over the surface of the print very gently with a little pad of cotton-wool.

The heating, if a hot bath is employed, must be so carried out as to produce no unevenness of temperature in the bath. The ideal method is to have the toning dish supported inside another dish without touching the bottom of that dish. This outer dish contains water, heated by a gas flame or other suitable means to the required temperature. Rougher methods, however, can be made to do very well if care be taken in regulating the source of heat.

The result obtained will vary with the original silver image. For fine dark brown tones, it is necessary that the original silver image should be decidedly too heavy and dark for a black print. This is not enough, however, to ensure success. The bath must

be thoroughly "ripe." The chief condition for ripeness is that the bath should contain sufficient silver; probably also long keeping contributes to this result. A quite new and unripened bath will reduce the prints considerably and tend to dissolve the half-tones, and will, moreover, only yield yellowish brown tones. It has been pretty well ascertained also that the brand of the paper and the previous history of the print make a considerable difference to the tone as well as to the time of toning.

Dr. Baekeland has recently pointed out that there is a danger to be reckoned with of the bath containing too much silver. When this occurs, the gelatine film of the print takes up some silver. Dr. Baekeland has named this "retained silver," and he states that he cannot accurately determine in what form this silver exists in the film. He finds that any retained silver may easily be detected after the print is washed and dried by touching the surface of the film on the white portion of the image with a drop of the solution of a soluble sulphide. A dark mark of silver sulphide is produced where this solution acts.

SULPHURETTING THE SILVER IMAGE.

B.—Indirect Methods.

It is much better, in my opinion, not to use the direct hypo-alum sulphuretting solution, but to rely entirely on the following indirect method. It is called indirect, because the silver image is first converted into one consisting of a silver haloid or of silver ferrocyanide, and then these easily sulphuretted bodies are converted into silver sulphide by treating the print with the solution of a soluble and suitable sulphide.

The method is far quicker and simpler to carry out than the hypo-alum method, and splendid dark brown tones can always be obtained easily and readily by its means, whereas the stage of ripeness of the hypo-alum bath must be exactly right for this bath to yield their equal, even if it can ever do so. Probably the results obtained by each are both equally permanent, but there is this to be said: The effect of the deposit of sulphur which takes place in the hypo-alum bath during toning may injuriously affect prints toned in this way—the question

is not by any means clear. Also there is the danger of retained silver, which has just been mentioned, awaiting the users of the ripest and best working baths.

The conversion of the silver image into one of a silver haloid or of silver ferrocyanide is usually referred to as "bleaching" the image. There are many solutions available for this purpose. From a purely chemical point of view, the best bleaching solutions to use are solutions of iodine, bromine, or chlorine in water—in the first case potassium iodide and in the second potassium bromide being added to promote solution. The chlorine and bromine solutions are not at all suitable for use, owing to the obnoxious vapours evolved. Iodine dissolved in potassium iodide solution is a most excellent bleaching solution. It is, in my opinion, when all things are considered, by far the best bleaching solution for subsequent sulphuration.

The following is a solution of suitable strength :

Iodine	.. ..	40 to 45 grains
Potassium iodide	..	110 „
Water	.. ..	to 10 ounces

The best way to make up the solution is first to dissolve the potassium iodide in about a fifth of the right amount of water, and then to add the iodine; and when this has dissolved to make up with water to the proper volume. A considerable quantity of the iodine solution should be made up at a time and stored in a large stoppered bottle. After using some of this solution, it should be poured back into the stock bottle. As the iodine solution becomes weakened by use, it should be replenished by the addition of solid iodine. By titrating some iodine solution with a solution of sodium thiosulphate of known strength before and after use, I have ascertained that the cost of the iodination of a 12in. × 10in. print is about one farthing.

The print before being immersed in the iodine or any other bleaching solution must be freed from hypo by thorough washing, and if it has been dried should be soaked in water till quite limp. In every case in which I have used the above iodine solution, complete bleaching has taken place in less than five minutes.

A point which may be noted about the

iodine bath is the effect it will have on any traces of hypo which may have remained in the fabric of the paper from the fixing bath. The result of the action between iodine and sodium thiosulphate (hypo) is that sodium iodide and sodium tetrathionate are formed. The sodium tetrathionate is probably quite as objectionable a compound as hypo itself; but still the disturbance caused by the reaction, there is good reason for believing, will aid in its elimination in the washing.

When the action of the iodine solution is complete, the image will appear pale yellow against a very deep blue ground. The blue colour is due to an addition compound formed by the iodine with the starchy constituents of the paper.

The next operation is to transfer the print straight from the iodine bath into a solution of sulphurous acid. The following will serve:

Sodium sulphite ($Na_2SO_37H_2O$)	..	60 grains
Sulphuric acid (concentrated)	.. ..	18 minims
Water	.. .. to	10 ounces

The print is left in this bath until the blue colour has been entirely destroyed, which is

very speedily accomplished. If it is now found that the bleaching has not been complete, the print is well rinsed, and is then put back into the iodine solution and left for a little time longer. It is then again treated with the sulphurous acid bath.

After treatment with sulphurous acid, the print is washed in running water, and is then ready for sulphuration. In the case of a print treated as described above, the washing in water between bleaching, or rather between clearing and sulphuration, need not be long. The object of the washing is to eliminate the sulphurous acid, and this is soon accomplished.

When dealing with large prints, and a considerable number of them at the same time, the fact that the inter-process washing in the case of the iodine bleacher is so readily and speedily carried out will be found a great practical convenience.

Before describing the sulphuretting operation, it will be convenient to consider some alternatives to the bleaching process just described. Instead of using sulphurous acid to discharge the blue colour caused by the iodine, sodium sulphite may be used. Its

use is not to be recommended, however, as it affects both the colour and depth of the resulting image, although this effect, which varies with the print and other circumstances, is sometimes so slight as not to be apparent. The cause of this phenomenon will be considered later. Potassium metabisulphite may be used, and the effect on the image is very slight indeed, even if there is any at all. Sulphurous acid has no effect certainly. If sodium sulphite is used, its solution should not exceed five per cent. in strength, and with all but the thickest papers two per cent. is sufficient. In this case, washing between clearing and sulphuretting is unnecessary.

In place of iodine, a good many solutions can be used for bleaching. Whatever is employed, the bleaching must be either quite even in depth all over the print, or else must be of such a depth all over the print that any further bleaching will make no difference to the tone. Provided that the latter of these two conditions is complied with, absolute completeness of bleaching need not be insisted on ; but, of course, it is much easier to tell when bleaching is complete than when it is sufficient, but still incomplete. With

regard to the first condition, this can very often be obtained, even when the bleaching has only to be carried to a slight degree all over the print; but unless one is prepared to spoil a fair number of prints, slight bleaching had better be left alone. Slight bleaching followed by sulphuration gives darker tones than more complete bleaching will, and certainly this is desirable in some cases. A safer method than slight bleaching to employ for obtaining darker tones will be described in the next chapter.

Any of the following solutions will be found to carry bleaching to a safe extent all over the print in about five minutes, and sometimes in less.

A. Potassium bichromate .. 90 grains
Sulphuric acid (concentrated) ..200 to 400 minims
Sodium chloride .. 1 ounce
Water .. .. to 10 ounces

This is the next best bleacher to the iodine solution. After its use the prints must be thoroughly washed in running water before sulphuration—washed till no yellow colour remains in the gelatine film. Washing in running water alone is sufficient; but should

this be found to take too long, an alum bath immediately after bleaching will expedite matters. Where cream crayon papers are being dealt with, the sulphuric acid had better not be increased beyond 200 minims in the above formula. The more sulphuric acid present the more rapid the bleaching. 200 minims is always sufficient, but this quantity can be doubled if preferred. For slight bleaching, this bath should be used diluted to about one-sixth of the above concentration. This is the best solution for attempting slight bleaching.

Potassium bromide can be substituted for sodium chloride in the above formula, using rather less. Such a solution, however, keeps badly—free bromine, which is objectionable, being soon formed. Of course, with free bromine present, the solution is a splendid bleacher from a chemical point of view. The chloride solution keeps very well for some months, and it should be stored in a bottle and used over and over again while it remains in good working condition.

B. Potassium ferricyanide.. 140 grains
Ammonium bromide .. 180 ,,
Water .. .. to 10 ounces

Potassium ferricyanide is itself a very slow and unsatisfactory bleacher, but the addition of an ammonium salt makes a lot of difference. The above solution will keep fairly well, especially in the dark, and it should be stored and used as described for the bichromate bleacher.

Washing after its use should be carried out in running water until all the yellow ferricyanide colour is removed before sulphuretting.

C.

Ferric chloride	90 grains
Hydrochloric acid (concentrated)	20 minims
Potassium bromide ..	200 grains
Water	to 10 ounces

This is, of course, a ferric bromide (and not chloride) bleacher, and yields silver bromide. After this bath, the prints will require to be washed in three or four changes of dilute sulphuric or hydrochloric acid before being washed in water, and this is a considerable objection to its use. If the acid treatment is not carried out, basic ferric salts are formed in the paper and film on washing in water.

Besides the above solutions, two others

perhaps ought to be mentioned, which have been suggested as means of converting a silver image into one of silver chloride or bromide for both development and sulphuration, viz., cupric bromide and cupric chloride. Suitable solutions can be made by dissolving half an ounce of copper sulphate in ten ounces of water and adding just a little sulphuric acid so as to form a clear solution, adding after this half an ounce of potassium bromide or of sodium chloride, as the case may be. Silver chloride and bromide are not formed by these solutions, but a mixture of silver haloid with the sub-haloid of copper is the result. Of course, the sub-haloids of copper are easily oxidised during the subsequent washing, and partially washed out; but for complete oxidation it is necessary to wash a bromide print brominated in this way for an hour or so. The long washing which is necessary after their employment makes these copper bleachers most inconvenient solutions to use where one wishes to have no copper compound left in the print before sulphuration.

A small quantity of copper sulphide in the image will not appreciably affect the

permanence of the resulting print, although copper sulphide is not under ordinary conditions as permanent a compound as silver sulphide. The presence of copper sulphide, however, introduces some uncertainty; its actual quantity will vary with the exact conditions prevailing during washing and with the time washing is continued.

A practical and convenient method of using the copper bleachers, but which will not eliminate all the copper, is to wash in running water for about ten minutes or a quarter of an hour after bleaching, then to immerse for a few minutes in a dilute solution of nitric, sulphuric, or hydrochloric acid—about one per cent. is a suitable concentration—and then after not more than five or six minutes, further washing in water to sulphuret the prints. The reason why the acid is used is to dissolve any basic insoluble cupric salts formed either from the cupric bromide or chloride solution carried over into the washing water with the print, or from the oxidation of the copper sub-haloid of the image. The reason why the second washing must be of limited duration is that it must not be prolonged sufficiently to form any

appreciable quantity of basic cupric salts by oxidising the remaining sub-haloid in the image, as if this happens the whites will be stained.

The visible effect of the copper left in the image on sulphuration is that the tone produced is a slightly warmer brown than would otherwise be the case.

Where the print is bleached for subsequent development, the copper bleachers should certainly not be used, for we most assuredly do not want to get any metallic copper mixed with the silver of the image, as metallic copper is by no means a permanent substance.

Now to consider the sulphuretting bath. The reagents which were at first employed for sulphuretting the bleached prints are :

(1.) Sulphuretted hydrogen.
(2.) Ammonium sulphide.
(3.) Yellow ammonium sulphide.
(4.) Potassium sulphurata B.P.

Sulphuretted hydrogen is excellent from the actual toning or chemical point of view, but its odour is exceedingly objectionable, and necessitates the operation of sulphuretting being conducted out of doors. Sulphuretted hydrogen gas escaping into the air

of a room will not only pervade the whole house with its most offensive odour, but will tarnish any silver plate, brasswork, or similar things, and will injure any photographic plates or silver printing papers with which it may happen to come in contact. The same objection, but to a somewhat less degree, applies to ammonium sulphide and yellow ammonium sulphide, as both these solutions evolve sulphuretted hydrogen. Potassium sulphurata B.P. contains hypo—a fatal objection to its use.

The sulphides of the alkaline earth metals do not offer very much help to the photographer in the indirect sulphuretting process. The monosulphides are the only sulphides of these metals at present on the market. Calcium monosulphide is not sufficiently soluble in water to be used for sulphuretting purposes. Strontium monosulphide is better, but of little or no practical value. Barium monosulphide is much the best of the three, and the only one to which a trial need be given. In making a sulphuretting solution from barium monosulphide, one should shake up one part of the sulphide with three hundred parts of water for a few minutes, and

then, after allowing any sediment to settle, should pour off the clear solution. The solution of barium sulphide is considerably hydrolysed, and so somewhat more odoriferous than that of sodium or potassium sulphide. It is quite a good sulphuretting reagent, however. As has just been said, the higher sulphides of the alkaline earth metals are not on the market, and besides being troublesome to make offer no particular advantages for sulphuretting purposes.

By far the best sulphuretting agents that are available for use are the pure monosulphides of sodium and potassium. Sulphuretting with these substances is speedy, even with very dilute solutions, and their use is attended by an almost complete absence of any unpleasant odour. At the present time there are on the market—

(1.) Fused potassium monosulphide (K_2S)

(2.) Fused sodium monosulphide (Na_2S)

(3.) Crystalline sodium monosulphide ($Na_2S.9H_2O$).

(4.) Crystalline sodium monosulphide purified for analysis ($Na_2S.9H_2O$).

It is the last of these substances which is recommended for toning purposes. It is the

purest form of alkaline sulphide which can at present be obtained.

The samples of fused potassium and sodium monosulphide which I have tested have all contained iron and a certain quantity of the polysulphides of potassium or sodium. On dissolving these substances in water, green solutions are formed. The green colour is due to the presence of a double sulphide of iron with sodium or potassium sulphide in the solution. On allowing the solution to stand for some time, or on boiling it, the iron is precipitated, and a yellow solution is formed in either case. The yellow colour is due to small quantities of the polysulphides of the metal. The presence of the polysulphides is of itself quite innocuous.

With one sample of fused sodium sulphide which I tested, I did not get good toning results. The prints toned with it were more reduced in density than they ought to have been, and the tones obtained were rather yellow. No doubt, in this case sodium thiosulphate was present. The only absolutely safe course it appears to me is always to use the *analytical reagent* $Na_2S.9H_2O$. This sub-

stance is not, as its name would imply, absolutely pure; but its only impurity is iron, which can easily be removed. After getting rid of the iron, the solution should be quite clear.

Slight yellowness in the case of a strong solution will very likely not matter. It is due to a small quantity of polysulphide. It shows, however, that the sample obtained is not of the very best quality, and there may possibly be a danger of thiosulphate contamination. When sulphur is fused with potash or soda, some thiosulphate is formed; and during the manufacture of sodium or potassium sulphide, such a reaction is very likely to occur if fusion is carried out.

With any form of sodium or potassium monosulphide, the solution as at first formed will be found to contain iron, and this iron should be got rid of before toning operations are commenced. The following is the best and most convenient way of making up the sulphuretting bath. Sodium monosulphide crystals, purified for analysis, are used, and of these three ounces are taken and dissolved in about threequarters of a pint of water. The solution at first formed is greenish,

owing to the iron present. The iron is present in varying amounts in different samples and in different crystals in each sample, but some is always present.

If this solution is allowed to stand for three or four days, all the iron will be precipitated as a black precipitate of ferrous sulphide. The solution may be boiled for about ten minutes in a glass beaker and then filtered, when all the iron is precipitated and left on the filter paper as ferrous sulphide. After the solution is cool, it is made up to twenty-five ounces with water. Of course, where boiling is not resorted to, the solution can be made up at once to twenty-five ounces. If boiling is not resorted to, the solution should be left to stand till it is colourless, and a black precipitate of ferrous sulphide lies at the bottom of the bottle. The precipitated ferrous sulphide does no harm, and so need not be filtered off, but filtration is certainly the neater proceeding.

Any sodium sulphide crystals, which are left over after making up the stock solution must be carefully corked up in their bottle, as the substance is very deliquescent. It

is a good plan to seal round and over the cork with melted candle-wax.

For the actual sulphuretting bath, the following are taken :

Twelve per cent. stock sodium sulphide solution, made up as above described	1 ounce
Water	12 to 20 ounces

After sulphuretting the print, it is washed thoroughly in running water. It should be left in the sulphuretting bath some little time after all visible change has ceased—say a total time of twice or three times as long as the visible change has taken for completion—and the conversion of all the silver haloid or ferrocyanide into sulphide will be complete.

It is better to use this bath quite dilute, because if the paper has a tendency to blister, the weaker the bath the less danger is there of blisters actually appearing. In cases where the emulsion has not taken the paper well, sodium sulphide solution has unfortunately the habit of causing blisters.

When the sulphuretting solution is pure, variation in the strength of the solution does not cause difference in the tones obtained.

As has been said above, the odour evolved from the sulphuretting bath is only very slight. What odour there is is due to slight hydrolysis of the sodium sulphide. This slight odour can be lessened by adding a small quantity of caustic soda to the sulphuretting bath ; but this proceeding may tend to produce blisters, and so it is better not to add any. If added, about one grain to the ounce can be tried at first, and more added afterwards if it is thought desirable and the paper will stand it.

The matter of iron in the sulphuretting bath is one that should always be looked to. Of course, if the crystals only contain a very little iron, it is not likely, especially if a dilute solution only is used, that any appreciable quantity of ferrous sulphide will be precipitated in the paper during the time of sulphuration. I have met with crystals containing a very large quantity, however, and so I certainly advise that all be got rid of before toning is carried out.

With three out of the five brands of cream crayon paper at present on the market, even when all the iron has been removed from the sulphuretting bath, a precipitation

of iron will be noticed to occur in the paper during sulphuration. The paper gradually becomes slightly greenish. The precipitation is caused by the action of the sodium sulphide on the colouring matter of the paper, which colouring matter is some compound of iron. The precipitation can be avoided by using sulphuretted hydrogen instead of sodium sulphide; but it is best to use sodium sulphide and to eliminate the iron sulphide afterwards, since sodium sulphide is a much more pleasant substance to use than hydrogen sulphide.

When a precipitation of iron sulphide is brought about on a print, no real harm is done, only we are put to somewhat more trouble than is otherwise the case. The prints must be washed in running water until no greenish tint remains. The ferrous sulphide oxidises, and partially washes out. There only remains a certain amount of basic ferric salts, and we may treat the print with a dilute solution of hydrochloric acid to get rid of this. The hydrochloric acid bath should be about 0.5 to one per cent., and is applied after washing in water, because otherwise some sulphuretted hydrogen would

be produced, and this is unpleasant. The only final visible result of the formation and removal of ferrous sulphide is that with the cream crayon papers, where the iron comes from the colouring matter of the paper the tint is slightly reduced. More ferrous sulphide is formed with the cream crayon papers if any of the previous solutions are strongly acid, so that if the bichromate-chloride bleacher be used, the minimum amount of acid given in the formula should be used. Of course, after the acid bath, the prints must be again washed in running water.

Finally, there are two very important points to be considered. If during bleaching, or at any time in the subsequent operations, there be present a solvent of silver compound, most objectionable results will occur. The case where such solvents are present in such amount as to act powerfully is easily understood, and is not likely to be met with. Here, of course, the density of the print finally obtained would be very seriously reduced, as well as the tone altered. However, less extreme cases may occur unless the sulphuretting process is so arranged as to avoid them entirely.

If sodium sulphite be used as a clearing agent after the iodine treatment, the final print obtained is both reduced in density somewhat and is altered in tone. The tone is rendered a more yellow shade of brown than it would otherwise be. A five per cent. solution of sodium sulphite is a solvent of silver iodide, but only to a very slight extent (the solubility being about one in twenty thousand). The effect of hypo or of any other thiosulphate in very small proportion in the sulphuretting bath is similar.

The action of the solvents appears to produce the following results, which results vary with the original silver image to some extent :

(1.) Reduction of density due to actual removal of the substance of the image.

(2.) Reduction of density due to molecular change in the substance of the image and loss of " covering power " thereby.

(3.) Alteration of tone—the brown tone is rendered more yellow. This is evidently due to some change in the molecular state of the substance of the image.

Rev. F. C. Lambert has pointed out an interesting case of this action. He finds

that if a print is bleached in a bath of potassium ferricyanide containing ammonia solution, reduction and yellowing of the image take place. If, however, sufficient potassium bromide is added to the solution, a normal result is obtained.

The explanation of the action of potassium bromide in preventing the solvent effect of the ammonia is too long to enter into here, but it can be found by any interested in the theoretical side of the matter in Prof. Walker's Introduction to Physical Chemistry (Macmillan & Co.) 2nd Edition pages 300-301 and again pages 309-311.

Some have advised these solvent methods as means of altering the tone. As, however, the solvent methods only render the tone more yellow than it would otherwise be, few will wish to do anything but avoid them. Whether a cold dark brown or a yellower one is preferred is, of course, a matter of taste; but a large majority will certainly aim at obtaining the former.

There are no "molecular" methods for darkening the tone. The best method of regulating the final tone obtained is to regulate the development. This brings us to by

far the most important part of the whole process—the original development.

Where no chance of solvent and molecular action is permitted anywhere in the process, and where bleaching is constant in depth, the image finally obtained is a function solely of the original silver image. To ensure success, then, a suitable silver image must be developed on the paper.

The covering power of silver sulphide is not equal to that of metallic silver, so that the image we must obtain must be darker and harder than when no toning is going to take place. Much over-exposure tends to yellowish tones. It is curious to note that a thin silver image yields not only a lighter but a yellower tone. The yellow effect is chiefly prominent when over-exposure has taken place, and a partial development with a dilute developer has been adopted. Splendid dark brown tones can be obtained by giving a fairly full exposure and developing out a dark vigorous image. It appears that it is best to use a strong developer for this purpose, although the chief point is to develop well out, and this can be done with a dilute one if long enough time is given.

The question of contrasts makes it impossible sometimes to avoid giving such a long exposure that it is not practicable to develop well out. Development must then be carried farther than when black tones are sought; but not quite such dark tones can ever be obtained as when a shorter exposure can be used.

Without claiming any special virtue for it, the amidol formula given in the first chapter can be thoroughly recommended.

VI.—MISCELLANEOUS METHODS.

WHEN sodium sulphide acts either on silver chloride, bromide, iodide, or ferrocyanide, the haloid or ferrocyanide of silver is entirely decomposed, and silver sulphide is formed quantitatively. When, however, Schlippe's salt (sodium thioantimonate $Na_3SbS_4.9H_2O$) is substituted for the sulphide, the above result does not occur. There is always some silver haloid or ferrocyanide left unchanged; and according to the percentage of the unchanged haloid or ferrocyanide, the colour varies. The colour also varies with the particular compound present.

In the case of the employment of a neutral solution of Schlippe's salt, a very considerable quantity of silver haloid or ferrocyanide remains unaltered, but with alkaline solutions much more, and perhaps in some cases all, of the original silver compound is converted into silver thioantimonate. The silver thioantimonate and the silver haloid or ferrocyanide do not appear to exist as a mere mechanical mixture, but seem to form some

sort of molecular compound or lake, which is stable when treated with sodium thiosulphate solution of ordinary fixing strength, but which is decomposed by a solution of sodium sulphide.

These lakes, or whatever they are, can be readily prepared and analysed.

An image composed of silver thioantimonate would no doubt be quite a permanent one; but as to images consisting of silver thioantimonate loosely combined or mixed with unstable silver compounds, the case is different. Such images are certainly far more open to attack by the traces of sulphuretted hydrogen in the air than a plain silver image is. Light does not seem to affect them, or, if it does so, the action is very slow.

What is the exact degree of permanence possessed by prints with these images can only be determined by practical experience; but on purely theoretical grounds they must be regarded with suspicion.

As has already been said, silver thioantimonate is a stable salt, but Schlippe's salt is very unstable. Even the carbon dioxide of the air decomposes it, forming sodium

sulphide, sodium thiosulphate, and antimony tri- and pentasulphides. The crystals are always covered with a crust of decomposition material, which must be washed off before use. The solution does not keep well, depositing sulphides of antimony.

In actual toning, the print, after being bleached, as in the indirect sulphuretting method already described, is carefully washed. When a neutral solution of Schlippe's salt is going to be employed, it is very important to see that no acid remains in the print, if, that is, any has been introduced during bleaching. In the case of the employment of a neutral bath, it is also important to remember that the concentration must not be great—about one per cent. is right—and that the print must not be washed in water immediately after the thioantimonate bath, but must be put first for a few minutes into a dilute solution of ammonia (about one-third per cent.) If these points are not seen to, a deposit of antimony sulphides will be certain to occur in the paper and film, thus fogging the whites.

The tones obtained by the employment of a neutral solution of Schlippe's salt are

various shades of red, reddish-brown, and yellowish-brown. They vary according to the special conditions prevailing. Very slight differences in these conditions make very considerable differences to the tone, probably influencing the extent to which the formation of silver thioantimonate proceeds.

Slight variation in the nature of the original silver image, other things remaining the same, seems to cause considerable variation in the tone obtained. Hence it is that the method is very uncertain, and so, even if the permanency of the image were above suspicion, it would not be of much practical value.

The addition of ammonia solution to the toning bath, by causing the action of the thioantimonate to go further, tends to the production of a darker and purer brown tone. The tone given is still a decidedly warm or yellowish brown, and the percentage of silver haloid or ferrocyanide is still considerable. The following solution can be tried :

Schlippe's salt ..	..	50 grains
.880 ammonia solution ..		20 minims
Water ..	.. to	10 ounces

After this bath, the print can be washed directly in water.

When a sufficient quantity of caustic potash or soda is added to the thioantimonate solution, it appears that in the case of an image consisting of silver chloride, bromide, or ferrocyanide, all or nearly all the silver is converted into silver thioantimonate. A suitable solution is :

Schlippe's salt	.. ..	60 grains
Caustic soda	.. ..	15 ,,
Water	.. ..	to 10 ounces

The solution will not keep long, and must be used soon after being made up, as if the caustic soda gets to any appreciable extent carbonated, the bath will not carry the reaction sufficiently far. Of course, in this case more caustic soda can be added, and this will put matters right again.

In case the tone given is thought not to be as dark as it should be if the reaction had gone to an end, more caustic soda can be added ; but too much of this reagent must not be employed, or the film will suffer.

The tones obtained are very similar to those of sulphuretted prints, but slightly more yellow in character.

It is difficult to say whether the reaction is absolutely complete. It is certainly very

nearly so, even if not quite so, when the thioantimonate bath is in good condition. In any case, the method can be employed with safety, but the sulphide method is better. Even with much larger quantities of caustic soda in the solution than given above, an iodine bleached print will not yield silver thioantimonate quantitatively; some silver iodide is always left unaltered.

By toning a print in a neutral solution of Schlippe's salt, and then immersing directly in a weak solution of sodium sulphide, various tones between a reddish or yellowish brown and a dark sepia can be obtained. The sodium sulphide acts on the unaltered haloid or silver ferrocyanide contained in the image, and converts this either partially or completely, according to the time of immersion, into silver sulphide; so by varying the time of immersion, different tones are obtained. After either this treatment or any of the alkaline thioantimonate baths, washing is carried out directly in running water.

It has been proposed to bleach a bromide print with a lead ferricyanide bleacher, and then to treat with Schlippe's salt. Here the same remarks apply as in the case of the

pure silver compounds, and the same methods can be used as suggested in their case.

A good lead ferricyanide bleacher is

Lead acetate	.. ..	90 grains
Potassium ferricyanide	..	140 ,,
Glacial acetic acid	..	150 minims
Water	to	10 ounces

The result of the action of this solution is that a mixture of silver and lead ferrocyanides is formed as the image. After bleaching is completed, the print must be washed in several changes of dilute acetic acid (about two per cent.) till the yellow colour is entirely removed from it. After this it must be washed in running water for sufficient time to get rid of the acid. The first washing in dilute acid is to prevent the formation of insoluble basic lead salts, which would cause stains.

Instead of employing Schlippe's salt after the lead bleacher, a reddish yellow tone due to the formation of chromates of silver and lead is obtained by treating the print with:

Potassium bichromate	..	1 ounce
.880 ammonia ..	..	1 ,,
Water	to	10 ounces

A purer yellow tone can be obtained by

using :

Potassium chromate .. 1 ounce
Water .. .. to 10 ounces

If a print is bleached with the well-known mercuric chloride bleacher, and then, after washing, treated with a sulphuretting solution, a warm black and considerably intensified image is the result.

The tone is too black for the method to be of much value for toning purposes, but the following modification will be found useful when dealing with weak prints as an alternative to the sodium sulphide method.

Weak greyish images do not yield, as has been seen, good results by the sulphuretting method ; the colour of the image is too yellow. In this case, bleaching the image only to a slight extent, and then sulphuretting, will certainly yield a better result than the normal method of complete, or practically complete, bleaching ; but, as has been said, this involves the danger of unevenness of tone, for if the bleaching is not even, toning will not be so either.

A better method in this case is to bleach pretty thoroughly—experience must teach the right amount of bleaching necessary—

with the bichromate chloride bleacher given previously diluted to about six times, and then, after thoroughly washing in running water, to complete the bleaching with a mercuric chloride solution. The following is recommended :

Mercuric chloride	..	90 grains
Hydrochloric acid (concentrated)	.. ..	50 minims
Water	.. .. to	10 ounces

After this solution, the print is washed in two or three changes of dilute hydrochloric acid (0.5 to one per cent.), and then in running water for about ten minutes or so. It is then sulphuretted in the sodium sulphide bath, as before described.

There is some doubt as to the action of a sulphuretting solution on a mercury bleached print. When a solution of a mercurous salt is treated with a soluble sulphide, a black precipitate is formed, and there is some doubt as to whether this is mercurous sulphide or a mixture of mercury and mercuric sulphide. In any case, the stability of a sulphuretted mercury bleached print will be found to be excellent.

Mr. C. W. Somerville has suggested treat-

ing a print toned in the copper ferricyanide toning bath with a solution of sodium sulphide. The tones obtained in this manner vary with the length of time during which the sulphuration is allowed to act, and also with the original copper tone. The action of the sodium sulphide seems to be quite evenly apportioned between the silver and the copper ferrocyanide. In the case of sulphuretted hydrogen, however, the silver ferrocyanide is attacked much the more readily, and so sulphuretted hydrogen would seem to be the most suitable solution to use for reddish browns.

The following can be tried :

Twelve per cent. stock sodium sulphide solution	¾ ounce
Sulphuric acid (concentrated)	30 minims
Water	to 10 ounces

It should be used out of doors. The tones obtained by this method vary between the red of the copper-toned print and the dark brown of an image consisting of copper and silver sulphide.

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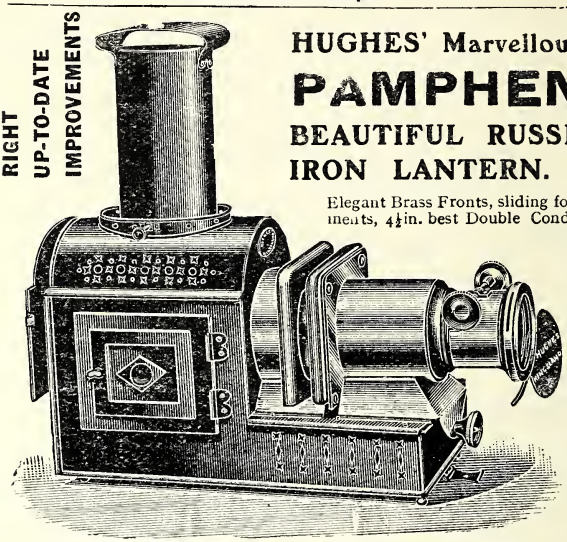

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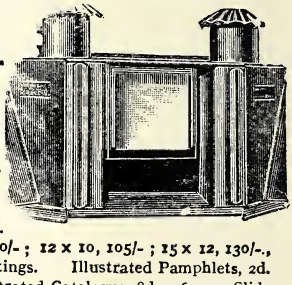

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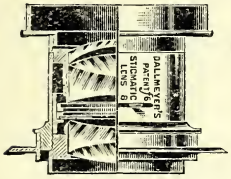

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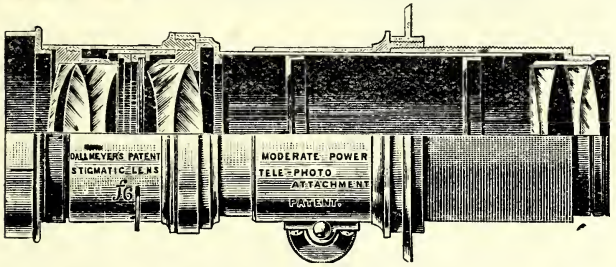

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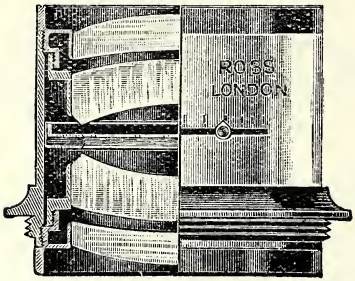

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